

**SOME CHEMICAL TRANSFORMATIONS  
STUDIED BY AB INITIO  
MOLECULAR ORBITAL CALCULATIONS**

**By**

**Gunnar Karlström**

lund 1978



SOME CHEMICAL TRANSFORMATIONS STUDIED BY AB INITIO  
MOLECULAR ORBITAL CALCULATIONS:

Gunnar Karlström  
civ.ing., Hb

AVHANDLING FÖR TEKNISK DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid en offentlig disputation i sal F, Kemicentrum, Lund, lördagen den 27 maj 1978 kl. 10.30.



Some Chemical Transformations Studied by ab initio  
Molecular Orbital Calculations.

by

Gunnar Karlström

Division of Physical Chemistry 2

Chemical Center P.O.Box 740

S-220 07 Lund

Sweden



THE CHINESE UNIVERSITY OF POLYMER SCIENCE  
AND TECHNOLOGY

CHINESE UNIVERSITY OF POLYMER SCIENCE  
AND TECHNOLOGY

CHINESE UNIVERSITY OF POLYMER SCIENCE  
AND TECHNOLOGY

CHINESE UNIVERSITY OF POLYMER SCIENCE  
AND TECHNOLOGY

CHINESE UNIVERSITY OF POLYMER SCIENCE  
AND TECHNOLOGY

CHINESE UNIVERSITY OF POLYMER SCIENCE  
AND TECHNOLOGY

SOME CHEMICAL TRANSFORMATIONS STUDIED BY AB INITIO  
MOLECULAR ORBITAL CALCULATIONS.

INTRODUCTION

Quantum chemical ab initio calculation has become an important tool in chemistry in the last 15 years. This new method has developed in close connection with modern computers. Originally quantum chemical methods were only applicable to small molecules, and usually molecular geometries and properties were calculated. This information could, however, be obtained by conventional experimental techniques, and the main achievement of this new method was perhaps to give information about the electronic structure of molecules. Quite often this knowledge could be used to explain the chemical transformations in which the molecule took part. The development of new computers, computational schemes and computer programmes have in the last 5-10 years made it possible to study chemical reactions between small molecules in a more direct way using ab initio quantum chemical methods.

The present work gives a summary of six articles all aiming in this direction. The first two are of methodological character whereas the last four deal with actual transformations of chemical interest: trying to extract information about the studied system that is difficult to obtain by other methods. The articles listed below will in the following be denoted by roman figures.

- I. A New Approach to Variational CI Calculations on  
Systems Containing Non-Interacting Molecules

Gunnar Karlström, *Theoretica Chimica Acta* 44,165-169  
(1977).

- II. A Critical Study of Basis-Set Effects and the Use of Approximate Natural Orbitals in SCF-CI Calculations of Molecular Geometries and Heats of Reactions. Gunnar Karlström, Bo Jönsson, Björn O. Roos and Per E.M. Siegbahn, *Theoretica Chimica Acta* In press.
- III. An Intramolecular Hydrogen Bond. Ab Initio MO Calculations on the Enol Tautomer of Malondialdehyde. Gunnar Karlström, Håkan Wennerström, Bo Jönsson, Sture Forsén, Jan Almlöf and Björn Roos. *Journal of the American Chemical Society* 97, 4188-4192 (1975).
- IV. Correlation Effects on Barriers to Proton Transfer in Intramolecular Hydrogen Bonds. The Enol Tautomer of Malondialdehyde Studied by SCF-CI Calculations. Gunnar Karlström, Bo Jönsson, Björn Roos and Håkan Wennerström. *Journal of the American Chemical Society* 98, 6851-6854 (1976).
- V. Multiconfigurational SCF and CI Calculations on the Open and Closed Form of the Ozone Molecule. Gunnar Karlström, Sven Engström and Bo Jönsson. Submitted for Publication.
- VI. Multiconfigurational SCF Calculations on  $\text{CH}_2\text{O}_2$ , an Intermediate in the Ozonolysis of Ethylene. Gunnar Karlström, Bo Jönsson and Sven Engström. Submitted for Publication.



The general method used in these articles is to calculate the total energy for the studied system as a function of some geometric parameters. In such a way a full or partial potential energy surface describing the studied transformation may be constructed.

### HISTORICAL PERSPECTIVE

The theoretical foundations of quantum chemistry were laid in the years of 1925 and 1926 when Heisenberg [1] and Schrödinger [2] presented their quantum mechanics. The following year (1927) Born and Oppenheimer [3] showed that the total wavefunction often could be separated into an electronic and a nuclear part. In 1930 Fock derived the well-known Hartree-Fock equations [4]

$$h^F \mu_1 = \varepsilon_1 \mu_1 \quad (1)$$

following the work of Hartree [5] and Slater [6]. In these equations  $h^F$  is a one-electron operator,  $\mu_1$  a one-electron wavefunction (an orbital) and  $\varepsilon_1$  the orbital energy. However  $h^F$  depends on the orbitals  $\mu_1$  in such a way that equation(1) actually represents a set of coupled integro-differential equations. In 1951 Hall [7] and Roothaan [8] realized that the problem of solving the Hartree-Fock equations could be simplified considerably, if the orbitals were expanded as a linear combination of some basis functions

$$\mu_1 = \sum_k c_{1k} \bar{\phi}_k \quad (2)$$

In this form, the problem of solving the Hartree-Fock equations was reduced to evaluating a set of integrals, and then diagonalizing a matrix (Fock-matrix) iteratively. The iterative procedure is needed since the form of the Fock-matrix depends

on the orbitals. Hopefully the procedure converges, i.e. the orbitals used to construct the Fock-matrix appears as the orbitals obtained by diagonalizing it. In this form the Hartree-Fock equations are extremely suitable for computer calculations, but not until 1966 did the first fairly general *ab initio* Hartree-Fock programs appear [9,10] .

### BASIC THEORY

In this work basically three different types of calculations will be discussed, all of *ab initio* type. The three types are one determinant closed shell self-consistent field (SCF) calculations, multiconfiguration self-consistent field calculations (MCSCF) and configuration interaction (CI) calculations. Below the elementary part of the theory on which these type of calculations are based, will be outlined.

#### The SCF-Method

For closed shell atoms and molecules the Hartree-Fock wavefunction is of the form

$$\Psi_e = \frac{1}{\sqrt{n!}} \begin{vmatrix} \mu_1(1) & \mu_2(1) & \dots & \mu_n(1) \\ \mu_1(2) & \mu_2(2) & \dots & \mu_n(2) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \mu_1(n) & \mu_2(n) & \dots & \mu_n(n) \end{vmatrix} \quad (3)$$

This is called a Slater determinant [6] and is often abbreviated

$$\Psi_e = A(n) \mu_1(1) \mu_2(2) \dots \mu_n(n) \quad (4)$$

$A(n)$  is an antisymmetrizing operator and  $\mu_i$  a spinorbital which may be written as a product of a spin function and a spatial orbital

$$\mu_i = \begin{cases} \chi_i & \alpha \\ \text{or} \\ \chi_i & \beta \end{cases} \quad (5)$$

A wavefunction according to equation (3) may be shown to obey the Pauli principle [11].

The spatial orbitals  $\chi_i$  can be assumed orthonormal

$$\int \chi_i(1) \chi_j(1) dv(1) = \delta_{ij} \quad (6)$$

and the same is true for the spin functions.

The total energy corresponding to a given wavefunction may always be calculated as an expectation value over the Hamiltonian operator of the system. Consequently the following expression for the total electronic energy may be obtained (in atomic units)

$$\begin{aligned} E_e = \int \Psi_e H_e \Psi_e d\tau = & \sum_i \int \mu_i^*(1) \left[ \frac{-\nabla^2}{2} - \sum_A \frac{Z_A}{r_{1A}} \right] \mu_i(1) dv(1) \\ & + \sum_{i,j} \left[ \iint \mu_i^*(1) \mu_j^*(2) \frac{1}{r_{12}} \mu_i(1) \mu_j(2) dv(1) dv(2) \right. \\ & \left. - \iint \mu_i^*(1) \mu_j^*(2) \frac{1}{r_{12}} \mu_j(1) \mu_i(2) dv(1) dv(2) \right] \end{aligned} \quad (7)$$

For closed shell atoms and molecules (7) can be further simplified. Using the fact that the Hamiltonian does not contain any spin-dependent terms one may obtain

$$\begin{aligned} E_e = & \sum_i 2I(\chi_i | \chi_i) + \sum_{i,j} \left[ 2(\chi_i(1)\chi_j(2) | \chi_i(1)\chi_j(2)) \right. \\ & \left. - (\chi_i(1)\chi_j(2) | \chi_j(1)\chi_i(2)) \right] \end{aligned} \quad (8)$$

where the abbreviations

$$I(\chi_i | \chi_j) = \int \chi_i^*(1) \left[ \frac{-\nabla^2}{2} - \sum_A \frac{Z_A}{r_{1A}} \right] \chi_j(1) dv(1) \quad (9)$$

and

$$(\chi_i(1)\chi_j(2) | \chi_k(1)\chi_l(2)) = \iint \chi_i^*(1)\chi_j^*(2) \frac{1}{r_{12}} \chi_k(1)\chi_l(2) dv(1) dv(2) \quad (10)$$

have been introduced.

In equation (8)  $\chi_i$  is a spatial orbital and the factor 2 comes from the spin integration. Inserting equation (2) into equation (8) gives

$$E_e = \sum_i \sum_k \sum_l 2c_{ik}c_{il} I(\phi_k | \phi_l) + \sum_i \sum_j \sum_k \sum_l \sum_m \sum_n (2c_{ik}c_{jl}c_{im}c_{jn} (\phi_k(1)\phi_l(2)|\phi_m(1)\phi_n(2)) - c_{ik}c_{jl}c_{jm}c_{in} (\phi_k(1)\phi_l(2)|\phi_m(1)\phi_n(2))) \quad (11)$$

The problem of solving the Hartree-Fock equations has now been reduced to that of evaluating a set of integrals over some basis functions and finding optimal values for a set of coefficients, under the condition that the orbitals should remain orthonormal, using the variational principle [12].

Basis functions most commonly used are of two types, Slater basis functions and Gaussian basis functions. These basis functions are generally centred on the nuclei and obtained from calculations on free atoms. The general form of the basis functions can be written

$$\begin{aligned} \phi_{\text{Slater}} &= f(r, \varphi, \theta) \exp(-ar) \\ \phi_{\text{Gauss}} &= f(r, \varphi, \theta) \exp(-br^2) \end{aligned} \quad (12)$$

All calculations discussed in this work are made with Gaussian basis functions.

### The CI-Method

The basic assumption leading to the Hartree-Fock equations for a closed-shell system is that the wavefunction may be written as a single Slater determinant. For many systems this is a good approximation, but in the general case the exact wavefunction must be written as an infinite sum of Slater determinants.

$$\psi_e = \sum_i c_i D_i \quad (13)$$



where  $c_i$  is a coefficient and  $D_i$  a Slater determinant, normalized such that

$$\int D_i D_j d\tau = \delta_{ij} \quad (14)$$

Naturally the infinite sum cannot be handled and a very common method for truncating the expansion is to use the orbitals obtained by an SCF-calculation, basing the expansion (13) on the HF determinant:

$$\psi_e = c_0 D_0 + \sum_{i,a} c_i^a D_i^a + \sum_{\substack{i,j \\ a,b}} c_{ij}^{ab} D_{ij}^{ab} + \sum_{\substack{i,j,k \\ a,b,c}} c_{ijk}^{abc} D_{ijk}^{abc} + \dots \quad (15)$$

Here  $D_0$  is the HF determinant and  $D_i^a$  is a determinant where orbital 'i' in the HF determinant is replaced with an unoccupied orbital (virtual) 'a', obtained in the SCF-calculation. Determinants  $D_{ij}^{ab}$ ,  $D_{ijk}^{abc}$  ... are constructed in a similar way. Usually the expansion (15) is truncated to contain only the first three terms.

The energy can now be calculated from

$$E_e = \frac{\int \psi_e^* H_e \psi_e d\tau}{\int \psi_e^* \psi_e d\tau} \quad (16)$$

Again applying the variational principle [12] to equation (16) it may be seen that one has only to determine the coefficients  $c_0$ ,  $c_i^a$  and  $c_{ij}^{ab}$  in such a way that the lowest possible energy is obtained.

When large basis sets are used in SCF-calculations many virtual orbitals are obtained. In order to speed up the convergence of expansion (15), in such cases the virtual orbitals may be transformed to approximate natural orbitals (ANO). The ANO's may be constructed in many different ways [13], all of which have in common that they attempt to reproduce the natural orbitals introduced by Löwdin [14] well. The natural orbitals can be shown to have optimal convergence properties in the full expansion proposed in equation (15).

### The MCSCF-Method

Many problems arise in ordinary CI-calculations.

The most important ones are: 1. The size of the problem increases rapidly with the size of the system studied. 2. The determinants in the expansion of the total wavefunctions are treated in a nonequivalent way, i.e. the orbitals are optimized for describing only the determinant corresponding to the HF wavefunction. This would not be a problem if the expansion contained all triple and higher substituted determinants, however due to the computational problems these determinants are usually not included. In particular when chemical reactions are treated, this is a serious problem.

The MCSCF-wavefunction is expanded as a sum of a few determinants (the most important ones to describe the system well), but both the orbitals and the coefficients by which the determinants contribute to the total wavefunction are simultaneously optimized.

### METHODOLOGICAL STUDIES

As was pointed out in the theory section the wavefunction in practically all ab initio calculations is expanded in a set of basis functions (basis set). Of course the accuracy of the results depends on the quality of the basis set. Let us consider briefly a chemical reaction  $A + B \rightarrow C + D$ . If the chosen basis set describes both products and reactants, as well as the entire reaction pathway equally well (with respect to the calculated total energy), the

potential energy surface obtained would be correct. Consequently it is the variation of the error with some geometry parameters that determines the reliability of a calculated potential energy surface. The goal of the methodological studies discussed in this work is to obtain information about the accuracy that could be expected with a given basis set, in a given type of calculation.

Energies calculated with a CI-wavefunction may naturally be added. However if the CI-wavefunction is restricted to include only singly and doubly replaced determinants with respect to the HF-determinant, the energy obtained for a system A plus the energy for a system B is not equal to the energy that would be obtained if the system (A+B) was treated in one calculation. The origin of this somewhat strange result is closely connected with the  $n$ -representability problem [15] . In fact, the quality of such a calculation depends on the size of the system. This means that only systems of equal size may be compared. For the reaction mentioned above this implies that the system (A+B) may be compared with the system (C+D) but in general no other comparison can be made. When calculating heats of reaction values for chemical reactions this causes problems. Quite often it is possible to handle the separate molecules A and B in separate calculations, but to treat both molecules in one calculation may be very difficult especially at the CI-level. In the first paper (I) discussed in this work this problem is solved in a way that gives variational energies,

very close to those obtained in a actual CI-calculation for the system (A+B), although calculations are only performed on the separated molecules A and B. This problem may also be solved in a different way by including the effect of higher substituted determinants according to Davidsons formula [16]. This method has the drawback, that it is not variational.

In the second paper (II) this method is used in an effort to investigate the reliability of a calculated potential energy surface (relative to the method and basis set used). Since heat of reaction values are experimentally well-known, such values are compared to calculated values. The products and the reactants corresponds to two points, which are taken as probes of the quality, of the calculated potential energy surface. The largest error in the calculated potential energy surface is probably larger than the error in the heat of reaction for the studied transformation. If several reactions are studied, it seems however reasonable to believe that a good estimate of the reliability of the calculated potential energy surface could be obtained.

In paper II the reliability of three different basis sets, ranging from a small double-zeta<sup>§</sup> to a good triple-zeta<sup>§</sup> basis, augmented with two polarisation functions<sup>§</sup>, is tested both at the SCF- and the CI-level. In the CI-calculations the efficiency of ANOs is also tested.

From the calculations presented in paper II one may conclude that for chemical reactions where the binding situation is drastically changed, i.e. breaking of bonds between first

§ Double-zeta means two basis functions per partially occupied orbital in the free atom, triple-zeta means three, and polarisation functions means basis functions with higher 'l' quantum number.



row atoms, a basis set better than double-zeta augmented with polarisation functions is needed, to obtain an error smaller than 10-15 kJ/mol. However for less drastic changes such a basis may be used. Further it may be concluded that CI-calculations, based on double-zeta basis sets, are of minor value for the estimate of heat of reaction values. In paper II it was also found that only a relative small part of the virtual space could be deleted in CI-calculations without loss of accuracy. Specifically it was found that if ANOs were constructed 20-30% of the virtual orbital space could be left out in the CI-calculation. For larger basis sets a relatively larger portion could be left out. In spite of the small reduction possible, ANOs may still be of value, since a reduction of the virtual space by 30% reduces the computational time by more than a factor of 2.5. Consequently for large basis set calculations, the ANOs may be a powerful tool for decreasing the computational effort.

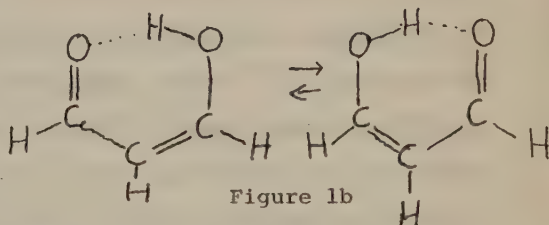
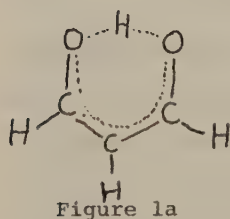
#### PROBLEM -ORIENTED STUDIES

As was mentioned in the introduction the general method used in these studies is to calculate a potential energy surface describing the chemical transformation of interest. Stable molecules are then located as minima and transition-states as saddle points in this surface. Usually this search is performed by fitting a polynomial in the varied geometry parameters to the calculated energy values. The actual search is then performed in the surface described by the polynomial.

#### Malondialdehyde

In papers III and IV malondialdehyde (MA), the parent compound

of  $\beta$ -diketones is studied. The problem investigated was whether the enol form of MA is best described according to figure 1a or as a rapid equilibrium between two topomeric forms indicated in figure 1b.



It is generally assumed that all common substituted (alkyl, aryl or fluorine substituents)  $\beta$ -diketones have the same structure in the enol form, and many experimental and theoretical efforts have been made to solve this problem. Some of the most interesting, from before the publication of III, are listed therein. Although the question was not settled at that time, most experimental data was interpreted in favour of a description according to figure 1a. The SCF-calculations performed with a double-zeta basis, presented in paper III, showed that MA is best described as indicated in figure 1b, and that the topomerisation barrier is 48 kJ/mol. In a later publication Isacson and Morokuma [17a] concluded also from SCF-calculations (performed with a smaller basis set (STO-3G)) that a description according to figure 1a is correct. Later Del Bene and Kochenour [17b] extended the work of Isacson and Morokuma to include a full geometry optimization with a STO-3G basis. In this way they showed that the discrepancy between the results of paper III and the study of Isacson and Morokuma was due to the limited geometry optimisation performed by Isacson and Morokuma. In III also two experimental methods

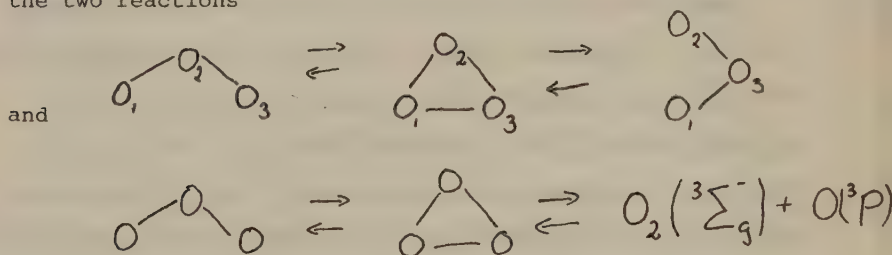
that may solve the problem were proposed: measurement of the quadrupole coupling constant for the hydrogen bonded proton and ESCA measurement of the oxygen 1s orbital energies. Later these experiments have been made [18,19] verifying the results of paper III. It is also interesting to note that the calculated structure has recently been supported by NMR-measurements of the isotope effect of the chemical shift of the hydrogen bonded proton [20], as well as by microwave spectroscopy [21].

The investigation presented in paper IV was undertaken in order to study the effect of dynamical correlation on the hydrogen bond in MA. Studies of smaller systems such as  $\text{H}_3\text{O}_2^-$ ,  $\text{HF}_2^-$  and  $\text{H}_5\text{O}_2^+$  had indicated that this factor could be of importance in such systems [22,23]. The main effect of the CI-calculations, performed with the same basis set as the SCF-calculations, and using a slightly truncated ANO-space, was to lower the topomerisation barrier from 48 to 42 kJ/mol and reduce the optimal oxygen-oxygen distance from 2.63 to 2.60 Å (experimental value 2.55 Å [21]). The theoretical value refers to the bottom of the potential energy well, and vibrational averaging will bring it closer to experiment.

It is possible now to state conclusively that the enol form of MA and related  $\beta$ -dicarbonyl compounds are best understood in terms of a rapid equilibrium between two topomeric forms. At this time only a quantum mechanical description of the actual topomerisation reaction in a given vibrational potential remains to be performed. One report along such lines have been published [24], unfortunately in a potential of low quality.

### The Ring and Open Forms of Ozone

The fifth article (V) discussed in this work concerns the ozone molecule. Originally it was planned as a methodological prestudy for the work described in the sixth article (VI). However the chemistry of the  $O_3$  system turned out to be quite interesting in itself. The structure of the ozone molecule has been known for a long time [25-27], however the existence of a cyclic form was recently postulated [28]. This form is assumed to serve as an activated complex for the two reactions



In paper V it is demonstrated that at least a basis set better than double-zeta plus polarisation function quality is needed to describe the energy difference between the two forms with an error less than 10 kJ/mol. Also the finding of other workers [29-31], that the ordinary  $O_3$  molecule must be described by at least a two configuration wavefunction at the SCF-level, is confirmed. However the most interesting studies concern the geometry of the ring form of  $O_3$ . Despite the molecule possessing  $D_{3h}$  symmetry at the one determinant SCF-level, inclusion of some of the correlation effects by performing MCSCF calculations, distorts the molecule, although the configurational choice was made in the full symmetry. In order to check these results we have performed a set of multiconfigurational CI (MCCI) calculations, i.e. CI calculations with many reference states in the rootfunction, using a double-zeta basis augmented with polarisation func-

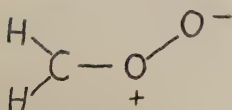


tions and others using only a double-zeta basis. Using the larger basis set only the two reference states with the largest coefficients could be included in the root function. This procedure actually destroys the symmetry of the molecule, but however already at the MCSCF-level the symmetry of the wavefunction is lower than the symmetry of the nuclear point group for  $D_{3h}$ -symmetric ozone, if the analysis is performed using  $C_{2v}$ -symmetry. Actually the use of  $C_{2v}$ -symmetry in the calculations on  $D_{3h}$ -symmetric ozone makes the O-O bonds non equivalent, which deforms the molecule. However if the analysis is performed using only  $C_s$ -symmetry all O-O bonds are equivalent and the molecule comes out  $D_{3h}$ -symmetric.

In paper V a bond length of 1.259 Å and a bond angle of  $116.1^\circ$  is deduced for the open form of ozone (experimental values 1.271 Å and  $116.8^\circ$  [27]). The corresponding calculated values for the ring form are 1.426 Å and  $60.0^\circ$ . The energy difference between the two forms are estimated to 120 kJ/mol and the transition-state between the two forms is placed 226 kJ/mol above the open form. These estimates, although somewhat uncertain places the ring form of  $O_3$  [32] 12 kJ/mol above its lowest dissociation products  $O_2(^3\Sigma_g^-)$  and  $O(^3P)$ .

### The Ozonolysis of Ethylene

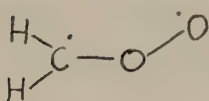
The ozonolysis of olefins has puzzled organic chemists for some 30 years. In 1949 Criege and Weiner [33] proposed that the reaction between ozone and an olefin passed via a zwitterion.



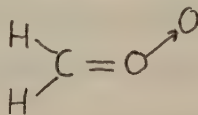
Methylene peroxide  
zwitterionic form

In paper VI methylene peroxide and some isomers have been studied by ab initio MCSCF calculations using a double-zeta basis augmented with polarisation functions. The aim of the study was to investigate the possible role of these isomers to serve as intermediates in the ozonolysis of olefins. The results obtained in the calculations supports the following conclusions.

1. Methylene peroxide is neither a zwitterion nor a singlet biradical (as proposed by Wadt and Goddard [34]), but a 'complex' between formaldehyde and a  $^1D$  oxygen atom.



Methylene peroxide  
biradical form



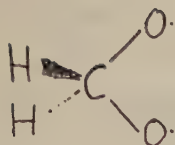
Methylene peroxide  
complex form

2. Methylene peroxide is rather unstable. It may dissociate to formaldehyde and a  $^1D$  oxygen atom without barrier, although  $\Delta E = 76$  kJ/mol, and it may probably rearrange to dioxirane.



Dioxirane

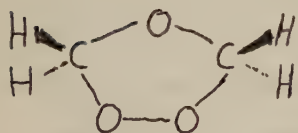
3. Dioxirane has recently been experimentally observed [35,36] and according to VI it is 118 kJ/mol lower in energy than methylene peroxide. The electronic structure of dioxirane is very similar to that of cyclic ozone. The somewhat too long O-O bond length observed 1.60 Å (experimental value 1.52 Å [35]) has probably a similar origin as the deformation of the ring form of  $O_3$  obtained in paper V. Further, it is found that there exists an equilibrium between dioxirane and an analog of ordinary ozone (dioxymethane).



Dioxymethane

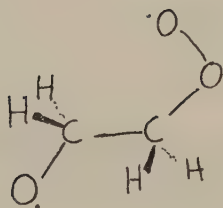
Dioxymethane is 7 kJ/mol higher in energy than dioxirane and the barrier to formation of dioxymethane is 64 kJ/mol.

4. Dioxymethane may react further to give carbon dioxide and a hydrogen molecule, with a barrier of 126 kJ/mol. It seems also most likely that dioxymethane rearranges to formic acid.
5. From the thermochemical data presented in paper VI, but also from isotopic labelling experiments [37,38] it seems less likely that dioxymethane or dioxirane will react with formaldehyde to form 1,2,4 trioxolane (secondary ozonide).

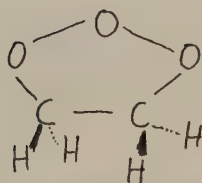


1,2,4 trioxolane

6. Due to the poor stability of methylene peroxide it seems less likely that 1,2,4 trioxolane may be formed from methylene peroxide and formaldehyde.
7. Since neither methylene peroxide, dioxymethane, nor dioxirane is likely to serve as an intermediate in the formation of 1,2,4 trioxolane, an open form of 1,2,3 trioxolane (primary ozonide) is proposed as the intermediate in this process.



1,2,3 trioxolane  
open form



1,2,3 trioxolane  
ordinary form

Such a form has been found to be only 25 kJ/mol above ordinary (closed) 1,2,3 trioxolane by Hiberty [39].

In fact from VI it seems less likely that the mechanism proposed by Criegee and Weiner 1949 should be a main reaction pathway in the ozonolysis of ethylene or related compounds. Also a slightly modified version of the Criegee mechanism where methylene peroxide is replaced by dioxirane or dioxy-methane seems inconsistent with the results presented in VI. Instead an open form of 1,2,3 trioxolane may serve as an intermediate replacing methylene peroxide in the Criegee mechanism.

ACKNOWLEDGEMENTS

First of all I wish to thank Sture since he encouraged me to start this work, but also for the light and free atmosphere which he has created on our department.

I also wish to thank Håkan, since he encouraged me to continue this work and guided me into quantum mechanics.

I am also largely indebted to Björn, Per and Janne, since they have made this work possible by constructing the MOLECULE program package.

Finally I wish to thank everybody mentioned above, but also Bo and Sven for valuable discussions.



# REFERENCES

1. W. Heisenberg, Z.Physik, 33,879(1925).
2. E. Schrödinger, Ann.Physik, 79,361,439(1926).
3. M. Born and J.R. Oppenheimer, Ann.Physik, 84,457(1927).
4. V.A. Fock, Z.Physik, 61,126(1930).
5. D.R. Hartree, Proc.Camb.Phil.Soc.Math.Phys.Sci.,  
24,89(1928).
6. J.C. Slater, Phys.Rev., 35,210(1930).
7. G.G. Hall, Proc.R.Soc., A202,328(1951).
8. C.C.J. Roothaan, Rev.Mod.Phys. 23,69(1951).
9. E. Clementi and D.R. Davies, J.Comput.Physics,  
2,223(1966).
10. J.G. Csizmadia, M.C. Harrison, J.W. Moskowitz,  
S. Seung, B.T. Sutcliffe and M.P. Barnell, The Poly-  
atom System, Technical notes 36 and 40, Cooperative  
Computing Laboratory M.I.T..
11. W. Pauli, Z.Physik, 31,765(1925).
12. H. Eyring, J. Walter and G. Kimball, 'Quantum Chemistry',  
Wiley, New York (1944).
13. E.R. Davidson, Advan. Quantum Chem., 6,235(1972).
14. P.O. Löwdin, Phys.Rev., 97,1474(1955).
15. A.J. Coleman, Rev.Mod.Phys., 35,668(1963).
16. S.R. Langhoff and E.R. Davidson, Int.J.Quantum  
Chemistry, 8,61(1974).

17. a) A.D. Isacson and K. Morokuma, J.Amer.Chem.Soc.,  
97,4453(1975).  
b) J.E. Del Bene and W.L. Kochenour, J.Amer.Chem.Soc.,  
98,2041(1976).
18. W. Egan, G. Gunnarsson, T.E. Bull and S. Forsén,  
J.Amer.Chem.Soc., 99,4568(1977).
19. R.S. Brown, J.Amer.Chem.Soc., 99,5497(1977).
20. G. Gunnarsson, H. Wennerström, W. Egan and S. Forsén,  
Chem.Phys.Letters, 38,96(1976).
21. W.F. Rowe Jr, R.W.Duerst, E.B. Wilson, J.Amer.Chem.Soc.,  
98,4021(1976).
22. a) Å. Stögård, A. Strich, J. Almlöf and B. Roos, Chem.Phys.  
8,405(1975).  
b) G. Diercksen, W. Kraemer and B. Roos, Theor.Chim.Acta,  
36,249(1975).
23. W. Meyer, W. Jakubetz and P. Schuster, Chem.Phys.Letters,  
21,97(1973).
24. S. Kato, A. Kato and K. Fukui, J.Amer.Chem.Soc.,  
99,684(1977).
25. R.H. Hughes, Phys.Rev., 85,717(1952), J.Chem.Phys.,  
21,959(1953), *ibid.* 24,131(1956).
26. R. Trambarulo, S.N. Ghosh, C.A. Burrus Jr. and W. Gordy,  
J.Chem.Phys., 21,851(1953).
27. T. Tanaka and Y. Morino, J.Mol.Spectrosc., 33,538(1970).
28. P.G. Burton and M.D. Harvey, Nature, 266,826(1977).
29. T.H. Dunning Jr. and W.A. Goddard III, J.Chem.Phys.,  
62,3912(1975).
30. P.J. Hay and T.H. Dunning Jr., J.Chem.Phys., 67,2290(1977).
31. L.B. Harding and W.A. Goddard III, J.Chem.Phys.,  
67,2377(1977).

32. Natl.Stand.Ref.Data Ser., Natl.Bur.Stand. 37(1971).
33. R. Criegee and G. Weiner, Justus Liebigs Ann.Chem., 546,9(1949).
34. W.R. Wadt and W.A. Goddard III, J.Amer.Chem.Soc., 97,3004(1975).
35. F.J. Lovas and R.D. Suenram, Chem.Phys.Letters, 51,453(1977).
36. R.I. Martinez, R.E. Huie and J.T. Herron, Chem.Phys. Letters, 51,457(1977).
37. C.W. Gillies, R.P. Lattimer and R.L. Kuczkowski, J.Amer.Chem.Soc., 96,1536(1974).
38. D.P. Higley and R.W. Murray, J.Amer.Chem.Soc., 98,4526(1976).
39. P. Hiberty, Chemical Institute of Canada/American Chemical Society 2nd Joint Conference 1977, Montreal Canada.





